

**Systematic catalyst design for selective methane to methanol
transformation: A computational approach**

Evangelos Miliordos

Auburn University

The selective functionalization of inert hydrocarbons has attracted major interest over the past decade. Terminal metal-oxygen bonds (MO) have been a common unit for many heterogeneous and molecular catalysts that insert oxygen in inert CH bonds. Here we present a systematic optimization of metal-oxide molecular catalysts for the conversion of methane to methanol by means of theoretical calculations. We used multi-reference calculations to harness the challenging electronic structure, and we followed a bottom-up approach to deal with the size complexity of these systems. We show that strong-field ligands stabilize the oxo form of MO (oxidative addition mechanism), and that weak-field ligands the more reactive oxyl form (radical mechanism). Metal oxides have been shown in the literature to oxidize methanol easier and thus cannot convert methane to methanol selectively. Here we show that metal oxide anionic species, as opposed to cationic or neutral, can interestingly serve as selective catalysts. In addition, the lessons from these calculations are applied to a new family of molecular catalysts, which contain a metal-methyl or metal-methoxide group. The guidance from our knowledge on metal oxide catalysts lead us to discover catalysts that bear higher activation barriers for the CH bond of methanol and thus prevent the overoxidation of methane.